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Application of Kramers–Kronig relations to the interpretation of dielectric data

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Abstract. The Kramers–Kronig transforms relating the real and imaginary parts of the dielectric susceptibility have been used both on empirical functions and on experimental data. Good agreement is found between measured values of the imaginary part and those calculated from measured values of the real part of the susceptibility.

1. Introduction

Under certain conditions that usually apply at low fields, the real and imaginary parts of the dielectric susceptibility ($\chi = \chi' - i\chi''$) are related by the Kramers–Kronig transforms. Hence, if only one component is known, the other may be found by applying a transform.

Dielectric loss peaks in solids are rarely of the classic Debye form but are usually much broader and often asymmetric when plotted with a logarithmic frequency axis. An empirical relation that fits a variety of materials (particularly organic polymers) is of the form (A K Jonscher 1974 private communication):

$$\chi'' = \frac{1}{(\omega/\omega_1)^{-m} + (\omega/\omega_2)^{1-n}} \tag{1}$$

where m and n lie between 0 and 1, and ω is positive. This increases as ω^m at low frequencies and decreases as ω^{n-1} at high frequencies (ie it reduces to a Debye peak if $m = 1$ and $n = 0$).

This paper describes the application of analytical and numerical transforms to empirical functions of this form and to experimental data.

2. Mathematical properties

The polarization of an isotropic dielectric in an electric field that varies sinusoidally with time may be described by a complex susceptibility

$$P = \epsilon_0 \chi E \tag{2}$$

provided that: (i) the amplitude of the polarization varies linearly with the amplitude of the field; and (ii) the polarization varies sinusoidally with time.

These requirements are satisfied if the polarization and the field obey a linear differential equation with constant coefficients. This is true for most materials at low fields.

The Kramers–Kronig relations may be derived by assuming that the principle of causality holds (Landau and Lifshitz 1960)

$$\chi'(\omega) = \frac{1}{\pi}\mathscr{P}\int_{-\infty}^{\infty} \frac{\chi''(u)}{u-\omega}\,\mathrm{d}u \tag{3}$$

$$\chi''(\omega) = -\frac{1}{\pi}\mathscr{P}\int_{-\infty}^{\infty} \frac{\chi'(u)}{u-\omega}\,\mathrm{d}u \tag{4}$$

where $\mathscr{P}$ means that the Cauchy principal value of the integral is used. χ' and χ'' are therefore Hilbert transforms of one another and belong to the class of conjugate functions (Titchmarsh 1959).

Now from the definition (2), together with the requirement that the values of P and E are real, it may be shown that $\chi'(\omega)$ is an even function whereas $\chi''(\omega)$ is an odd function. Hence the relations may also be expressed as

$$\chi'(\omega) = \frac{2}{\pi}\mathscr{P}\int_{0}^{\infty} \frac{u\chi''(u)}{u^2-\omega^2}\,\mathrm{d}u \tag{5}$$

$$\chi''(\omega) = -\frac{2\omega}{\pi}\mathscr{P}\int_{0}^{\infty} \frac{\chi'(u)}{u^2-\omega^2}\,\mathrm{d}u \tag{6}$$

which are more useful in practice.

3. Analytic solutions

A special case of (1) that can be transformed exactly is with $m = n$

$$\chi'' = \frac{\omega^n}{1+\omega}.$$

A number of materials give loss-peaks similar to this with $n \simeq 0{\cdot}7$ (A K Jonscher 1974 private communication). The real part of the susceptibility is

$$\chi' = \frac{1}{(\omega^2-1)\tan\frac{1}{2}n\pi}\left[\omega^n(\omega\tan^2\tfrac{1}{2}n\pi + 1) - (\tan^2\tfrac{1}{2}n\pi + 1)\right]$$

and this is shown for $n = 0{\cdot}7$ in figure 1.

At high frequencies, the ratio χ'/χ'' tends to the value $\tan\frac{1}{2}n\pi$ that holds if $\chi'' = \omega^{n-1}$ at all frequencies. For $n = 0{\cdot}7$ the ratio is within 5% of the value $1{\cdot}96$ $(= \tan\frac{1}{2}(0{\cdot}7\pi))$ for frequencies greater than ten times that at which the peak of χ'' occurs.

4. Numerical solutions

4.1. Broad loss-peaks

The empirical expression for broad, asymmetric loss-peaks (1) may be given in the reduced form

$$\chi'' = \frac{\omega^m}{A + \omega^{m-n+1}}$$

which may be transformed numerically. An outline of the method of computation is given in the Appendix.

The result of applying the transformation to a broad loss-peak with $m = n = 0{\cdot}7$ is identical with figure 1. The transformation for a rather narrower peak ($m = 0{\cdot}8$, $n = 0{\cdot}2$) is shown in figure 2.

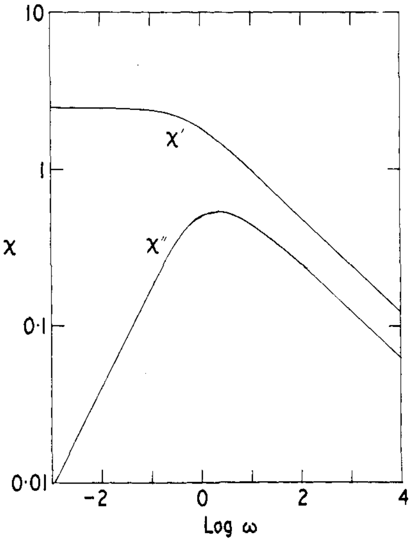

Figure 1. Exact transformation from χ'' to χ' for $\chi'' = \omega^n/(1 + \omega)$ with $n = 0{\cdot}7$.

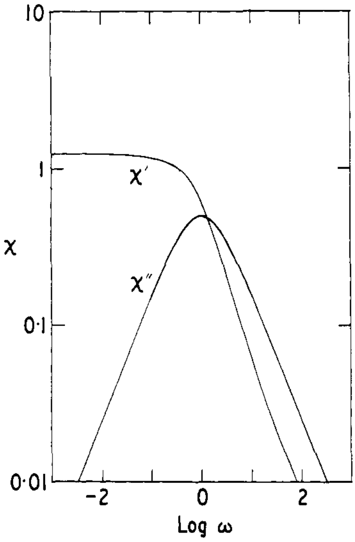

Figure 2. Numerical transformation from χ'' to χ' for $\chi'' = \omega^m/(1 + \omega^{m-n+1})$ with $m = 0{\cdot}8$ and $n = 0{\cdot}2$.

4.2. Experimental data

Kramers–Kronig transformations of experimental data are useful in a number of situations:

(i) since measurements of χ' do not include the delta function at $\omega = 0$ due to the DC conductivity, χ'' calculated from them does not contain the contribution from the DC conductivity and thus new loss-peaks may be found at low frequencies;

(ii) the part of χ' due to a particular polarization mechanism may be found from measurements of χ'' near the corresponding peak; and

(iii) agreement between experimental and calculated values gives more confidence in the results.

Experimental data differ from mathematical functions in containing random errors and only extending over a limited frequency range.

The effect of errors depends on the form of the χ against ω characteristic. For example, even one small error in a χ' that is almost independent of frequency will give a peak in χ''. Smoothing the data would reduce the effect but could hide true features. Various criteria may be used to find true errors:

(i) for frequencies less than 10^{10} Hz, all loss processes are likely to be relaxations, that is, $d\chi'/d\omega$ should be negative;

(ii) a gradient of log χ' against log ω steeper than -2 is unlikely, as is a gradient of log χ'' against log ω lying outside the range -1 to $+1$; and

(iii) data are also suspect if the gradient of lines joining consecutive points changes sharply from one interval to the next. Random errors are less important for data that are closely spaced in frequency.

Since the value of χ'' (say) at a given frequency depends on values of χ' over a range of frequencies near the given one, it is necessary to extrapolate χ' outside the range of measurements to calculate χ'' near the extremes of the range. The method used in the

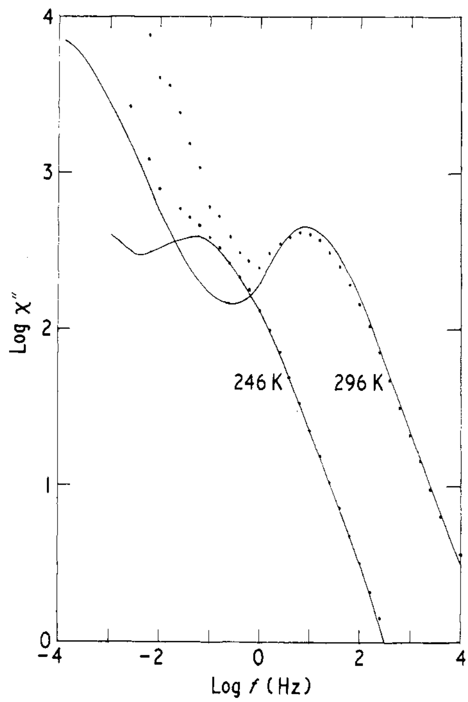

Figure 3. Comparison of experimental χ'' and curves from numerical transformation of χ' (STAG II—$Si_{21\cdot3}Te_{43}As_{26\cdot8}Ge_{8\cdot9}$).

present work is to fit a least-squares straight line to the first (or last) few points on a log χ against log ω plot and this line is used over the decade of frequency below the first point (or above the last point). χ' is taken to be constant (or χ'' is taken to be zero) outside this range and χ'' (or χ') is only calculated for frequencies within the range of the measurements. For accurate results, the points should extend over at least three decades of frequency. An outline of the method of computation is given in the Appendix.

Transformations of results for a STAG glass are shown in figure 3. It can be seen that there is good agreement with the experimental χ'' at high frequencies and that the AC component of χ'' is recovered at low frequencies.

In organic polymers, the loss usually varies much less with frequency. A transformation of typical polymer data (nylon 610: Curtis 1961) is shown in figure 4. It can be seen that at low frequencies the difference between the measured and calculated χ'' gives a good straight line with a slope of -1 ($\log \chi''$ against $\log f$), as expected for the DC component of χ''.

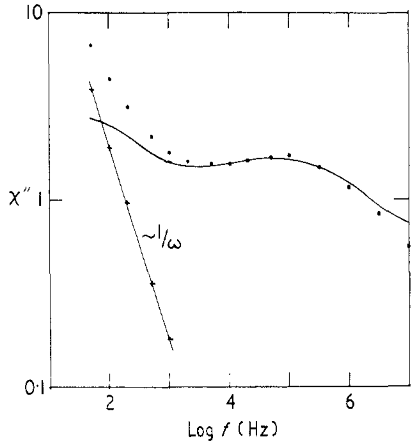

Figure 4. Comparison of experimental χ'' and curve from numerical transformation of χ' for nylon 610 at 80·7°C (data from Curtis 1961). ● experimental χ''; + difference between experimental and calculated χ''.

5. Conclusions

The work has shown how the Kramers–Kronig relations can be used in practical studies of dielectrics at low frequencies. Numerical transforms may be used for empirical functions that cannot be transformed exactly. Experimental data may also be transformed numerically provided that they extend over at least three decades of frequency.

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Appendix

(*a*) *Transformation of empirical functions*

The first step in transforming to $\chi'(\omega)$ is to integrate across the singularity at $u = \omega$. This is done by approximating χ'' by the line

$$\chi''(u) = au + b$$

from slightly below $u = \omega$ to slightly above $u = \omega$. This gives the exact integral:

$$\int_{u_1}^{u_2} \frac{u\chi''(u)}{u^2 - \omega^2} \mathrm{d}u = a\left[(u_2 - u_1) + \frac{\omega}{2}\ln\left|\frac{\omega - u_2}{\omega - u_1}\frac{\omega + u_1}{\omega + u_2}\right|\right] + \frac{b}{2}\ln\left|\frac{\omega^2 - u_2^2}{\omega^2 - u_1^2}\right|.$$

A subroutine is used to integrate over the rest of the range. Since χ'' is significant over a wide frequency range, the integral is used in the form

$$\int \frac{\chi''(u)}{1 - \omega^2/u^2} \, \mathrm{d}(\ln u).$$

This is evaluated using Simpson's rule with equal increments of ln u. The subroutine integrates over one decade (or part of a decade) at a time in the following order:

(i) the rest of the decade below 10ω using 100 increments;
(ii) the rest of the decade above $0{\cdot}1\omega$ using 100 increments;
(iii) the decades above 10ω using 10 increments, continuing until a decade gives a negligible contribution; and
(iv) the decades below $0{\cdot}1\,\omega$ using 10 increments, continuing until a decade gives a negligible contributjons.

All the contributions are then added and multiplied by $2/\pi$ to give $\chi'(\omega)$.

(b) Transformation of experimental data

To apply simple methods of integration to unequally spaced data, it is necessary to interpolate between the points. Since dielectric data are typically very smooth when plotted as ln χ against ln f, the method used in the present work is to fit exact parabolae

$$\ln \chi(f) = A(\ln f)^2 + B \ln f + C$$

to sets of three consecutive points (in most cases the parabolae will be almost straight between the three points).

Least-squares straight lines

$$\ln \chi(f) = B \ln f + C$$

are then fitted to the first (or last) few points.

The method of transforming this approximating function is similar to the previous one except that intervals between alternate points are used instead of decades.

The approximation near the singularity is exactly the same, the corresponding expression for transforming to $\chi''(f)$ being

$$-\int_{u_1}^{u_2} \frac{f\chi'(u)}{u^2 - f^2} \, \mathrm{d}u = -\frac{af}{2} \ln\left|\frac{f^2 - u_2^2}{f^2 - u_1^2}\right| - \frac{b}{2} \ln\left|\frac{f - u_2}{f - u_1}\frac{f + u_1}{f + u_2}\right|.$$

The subroutine for transforming to $\chi'(f)$ is similar to that used before, whereas for transforming to $\chi''(f)$ the integral is used in the form

$$-\int \frac{\chi'(u)}{u/f - f/u} \, \mathrm{d}(\ln u).$$

The integrals are evaluated using Simpson's rule with equal increments of ln u, the number of increments being chosen to give about 50 per decade. We define an interpolating interval to be the region in which a single interpolating equation is used (eg the interval between the first and third points or the interval between the highest frequency and ten times the highest frequency). The subroutine integrates over one interval (or part of an interval) at a time in the following order:

(i) the remainder of the interval below u_1 $(=0{\cdot}8f)$;
(ii) the remainder of the interval above u_2 $(=1{\cdot}25f)$;

(iii) the rest of the intervals above f, stopping if an interval gives a negligible contribution; and

(iv) the rest of the intervals below f, stopping if an interval gives a negligible contribution.

For transforming to $\chi'(f)$, we assume that $\chi''(f)$ is zero outside $0{\cdot}1f_1$ to $10f_N$ (where f_1 is the lowest frequency and f_N is the highest frequency). Hence the sum of all the contributions so far multiplied by $2/\pi$ gives $\chi'(f)$.

For transforming to $\chi''(f)$, we assume that $\chi'(f)$ takes the end of range values outside $0{\cdot}1f_1$ to $10f_N$ and hence there is an extra contribution:

$$-\frac{2f}{\pi}\left[\chi'(0{\cdot}1f_1)\int_0^{0\cdot 1f_1}\frac{\mathrm{d}u}{u^2-f^2}+\chi'(10f_N)\int_{10f_N}^{\infty}\frac{\mathrm{d}u}{u^2-f^2}\right]$$

$$=-\frac{1}{\pi}\left[\chi'(0{\cdot}1f_1)\ln\left(\frac{f-0{\cdot}1f_1}{f+0{\cdot}1f_1}\right)-\chi'(10f_N)\ln\left(\frac{10f_N-f}{10f_N+f}\right)\right].$$

where $\chi'(0{\cdot}1f_1)$ and $\chi'(10f_N)$ are obtained by extrapolation using the least-squares straight lines. Adding this to $2/\pi$ times the sum of all the other contributions gives $\chi''(f)$.

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